

Electrochemical Behavior of Surface-Modified Natural Graphite for High-Power Applications

J. Liu, C.H. Chen, J.S. Luo, D. P. Abraham, D. R. Vissers, and K. Amine

Electrochemical Technology Program,
Chemical Technology Division,
Argonne National Laboratory, 9700 South Cass Ave.
Argonne, IL 60439

Carbon materials are commonly used as the negative electrode in lithium-ion cells. Among the various carbon materials, natural graphite shows the most promise because it has a high capacity (372 Ah/kg), low redox potential, relatively flat potential profile, and low cost. However, the use of natural graphite is limited by its sensitivity to certain electrolytes. For example, graphite electrodes are not compatible with propylene carbonate (PC)-based electrolytes, which have a lower melting point and better safety characteristics. The problem is that solvent molecules of the electrolyte co-intercalate with Li^+ into the graphite, frequently leading to the exfoliation of the graphite matrix.

In this effort, surface-modified natural graphite [1,2] was obtained from Mitsui Mining Co. Ltd., the surface had been modified by a thermal vapor deposition (TVD) technique. The performance of the TVD-coated graphite in PC-based electrolytes was evaluated under the high-power test conditions that were developed under the Partnership for a New Generation Vehicles (PNGV) program.

To visualize amorphous carbon at the surface of natural graphite, individual graphite particles were embedded in resin and sectioned by a Reichert-Jung Microtome to yield ~50-nm thick samples for examination by transmission electron microscopy (TEM). High-resolution TEM was carried out with a JEOL 4000EX microscope operating at 400 kV. A representative TEM image from a cross section of the carbon-coated graphite particle is shown in Fig. 1. The carbon coating displayed a disordered crystal structure; electron diffraction patterns obtained from the coating contained rings, which confirmed the amorphous nature of the coating. In contrast, the bulk side of the particle had a layered structure; diffraction patterns taken from the bulk had spots that were typical of the graphite crystal structure.

The charge curves of 3.8 and 7.6 wt% carbon-coated graphite are shown in Fig. 2. In the 3.8 wt% carbon-coated sample, the early part of the first charge curve displays a wavy nature with two plateaus observed near 0.8 V, which indicate typical exfoliation behavior in the PC-based electrolyte. In the thicker coated sample (7.6 wt%), however, there is no exfoliation during the initial charging of the cell, even when using a high concentration (70 wt%) of PC in the electrolyte.

Similar results were observed with 13 and 17.6 wt% carbon-coated samples. All charge curves displayed plateaus below 0.2 V that can be attributed to lithium intercalation into the graphite matrix.

The hybrid pulse power characterization (HPPC) test was performed on cells with graphite anodes and PC-based electrolytes in accordance with the procedure described in the PNGV test manual [3]. Figure 3 shows a typical HPPC test result. This cell had $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ as the positive active material and carbon-coated natural graphite as the negative active material. Both positive and negative electrodes were engineered with the aim of reducing cell resistance and increasing power.

The cell was initially charged at the 1C rate, followed by a sequence of 18-s high-rate discharge pulses (10C rate) and 10-s regenerative charging pulses (2-s pulse at 8C rate, and 8-s charge pulse at lower rate). This

sequence was repeated every 10% depth of discharge [3].

Figure 3 shows the area specific impedance (ASI) for the HPPC 18-s discharge and 2-s charge pulses as a function of depth of discharge(DOD). The ASIs for both charge and discharge are very low over a wide range of DOD. These values are lower than the ASIs, needed to meet the PNGV performance goal, which is 35 $\text{ohm}\cdot\text{cm}^2$ for 18-s discharge and 25 $\text{ohm}\cdot\text{cm}^2$ for 2-s charge pulses. The cell pulse-power capability for both charge and discharge was thus found to meet the PNGV power requirement, especially in the “sweet spot” of 30-70% DOD.

The above results indicate that cells containing the surface-modified natural graphite will meet the power requirement set by the PNGV for the hybrid vehicle application. This anode material will allow for the use of a high performance and stable PC-based electrolyte that could improve the safety, calendar life, and the cost of the lithium ion battery.

Acknowledgment

The authors acknowledge Mitsui Mining for providing TVD carbon-coated samples and DOE's Office of Advanced Automotive Technologies for its financial support under contract No. W-31-109-ENG-38.

References

- [1] M. Yoshio, H. Wang, K. Fukuda, Y. Hara and Y. Adachi, J. Electrochem. Soc., **147** (4), 1245 (2000).
- [2] H. Wang and M. Yoshio, J. Power Sources, **93**, 123 (2001).
- [3] “PNGV Battery Test Manual”, Revision 1, Idaho National Engineering Laboratory, Department of Energy, DOE/ID-10597 (May, 1998).

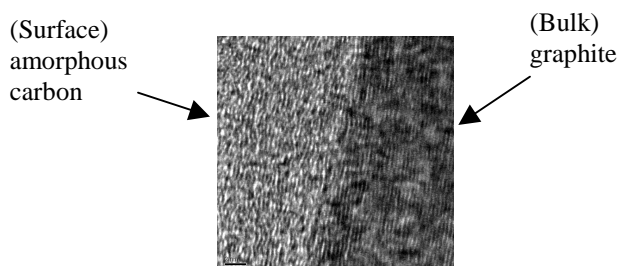


Fig. 1. TEM of cross section of carbon-coated graphite particle.

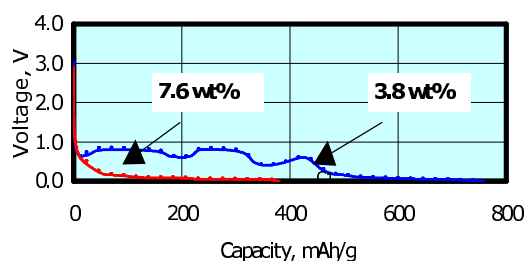


Fig. 2. Charge curves of 3.8 and 7.6 wt% carbon-coated graphite electrode. Electrolyte is 1M LiPF_6 / 70 wt% propylene carbonate and 30 wt% ethylene carbonate.

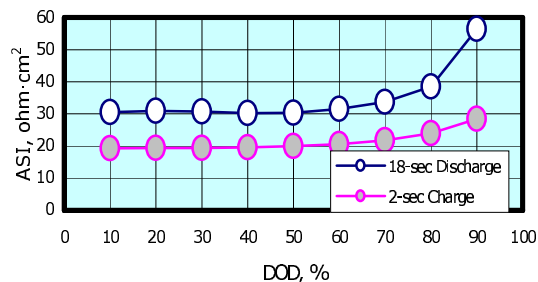


Fig. 3 ASI vs. DOD for cell using 13 wt% carbon-coated graphite. Electrolyte is 1.2M LiPF_6 /EC/PC/MEC/DEC (20:50:20:10).